

# **Quantitative and Qualitative Prediction of Light Absorption by Colored Dissolved Organic Matter in the Coastal Zone**

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## **LONG-TERM GOALS**

To produce a physical water mass mixing model for describing colored dissolved organic matter (CDOM) distributions in the coastal zone. The model will combine the effects of local non-conservative processes with overall mixing of major CDOM end-members from terrigenous and marine sources. Although the model will be firstly derived for one study site (the entrance to the Baltic Sea) the approach will be designed for implementation in other regions of Navy interest (international estuaries and harbors).

## **OBJECTIVES**

This project will provide a tool for predicting the quantitative and qualitative distributions of CDOM in the littoral zone based on combined model of CDOM biogeochemical cycling and physical oceanography. This approach provides the Navy with an alternative technique by which to gauge the performance of satellite based predictions of CDOM distributions. A major focus of this software will be the removal of CDOM “noise” in riverine and estuarine environments.

## **APPROACH**

The study area is the Baltic Sea-North Sea mixing zone at the entrance to the Baltic Sea (Figure 1). The Baltic Sea is a large enclosed sea bordering 10 different countries, strategically important to NATO and Northern Europe. The major shipping entrance into the Baltic is through the Danish straits. There is additionally access through the Kiel Canal (Germany); however, access is limited. The Baltic Sea is a large estuary with the processes influencing CDOM during saline mixing in the Danish straits being the same as those for other estuaries (e.g. flocculation and microbial/photochemical degradation). The Baltic Sea is strongly influenced by freshwater inflow due to its large drainage basin ( $1.63 \times 10^6 \text{ km}^2$ ) and limited exchange with the North Sea (Atlantic Ocean). As a result its waters have a high content of terrestrially derived organic material.

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***Figure 1. Map of the Baltic sea indicating the countries that border it. The red square indicates the proposed study site; the Baltic-North Sea mixing zone.***

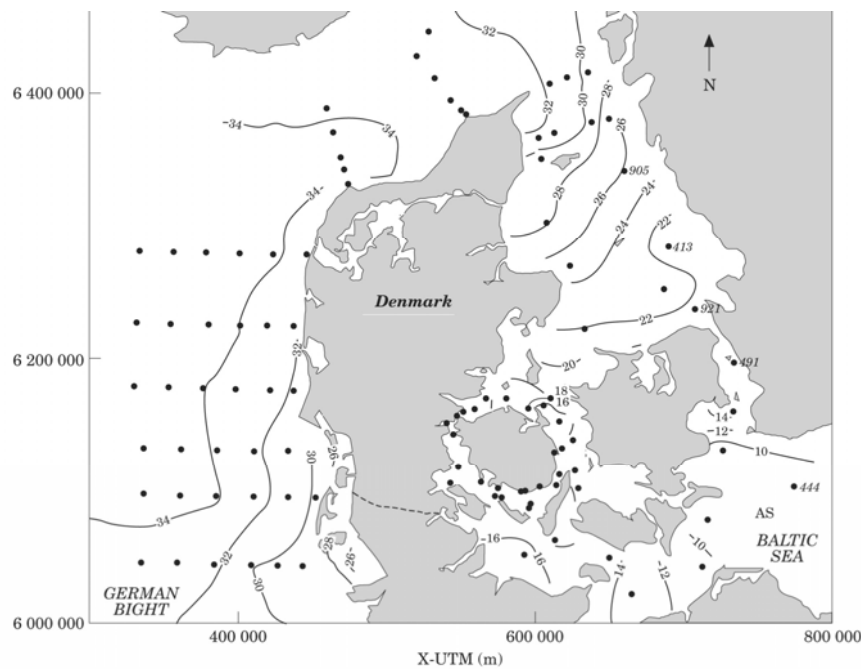
This study site was chosen in order to utilize the numerous sampling opportunities from the Danish National monitoring program (nationally funded) and the existing implementation of 3D physical mixing models in the region by NERI. However the emphasis in this project is on the applicability of this approach to estuaries and coastal zones globally. For example the same model is being currently being applied by NERI in projects on the east and west coasts of Greenland.

The project has three work packages.

#### *Work Package 1-Collection of a calibration data set*

In order to achieve the goals of this project a comprehensive foundation of the seasonal variations in CDOM in these waters is needed. Although we already have a large degree of understanding of the processes controlling CDOM distributions in these waters (e.g. Højerslev et al 1996; Stedmon et al 2000), several contributing factors remain unknown. First, it is vital to have good seasonal coverage of CDOM variations in the region to accurately gauge the extent of this variability for these waters. The concentrations and characteristics of CDOM in the freshwater run-off varies with season (Stedmon and Markager 2005). Additionally, in spring and summer there is production of CDOM associated with phytoplankton productivity in the surface waters, although the importance of this source relative to terrestrial CDOM is currently not known. Finally, Boyd and Osburn (2004) have shown that salinity may alter the biological and photochemical reactivity of CDOM, affecting its concentration and characteristics.

The sampling strategy is coordinated with the Danish National Monitoring Program, which is based at NERI (Figure 2). NERI runs five cruises a year covering the whole study site. The cruises are in February, August, September, October and November. The February cruise is useful for studying the winter conditions where water mass mixing controls CDOM distribution. The summer to fall cruises will provide important information on the autochthonous production and degradation (photochemical and microbial) with time, of CDOM associated with summer phytoplankton productivity. (Responsible project partner: NERI, with some participation by NRL)



**Figure 2** Close up of proposed study area at the entrance to the Baltic Sea. Refer to Figure 1 for location. Dots on the map indicate monitoring stations from the Danish National Monitoring program which will be used. Contour lines indicate the salinity gradient of the mixing zone between the freshwaters of the Baltic Sea to the East and the saline North Sea to the West. (Figure adapted from Stedmon et al 2000).

Measurements of the light absorption and fluorescence properties of CDOM will be made. Additionally recently developed detailed fluorescence spectroscopy techniques that characterize CDOM will be applied (Stedmon et al 2003). (Responsible project partner: NERI)

Detailed chemical measurements will be used to describe the composition and hence source/extent of reprocessing of the organic material. These measurements will include carbon, nitrogen and phosphorus content (DOC, DON and DOP), stable isotopic composition of DOM, and lignin content (Osburn et al 2001). (Responsible project partner: NRL)

This work package will provide insight to the underlying chemical compositional variations in CDOM leading to changes in its absorption spectra. Basic oceanographic parameters (temperature and salinity) and other water quality data (e.g. Secchi depth, diffuse attenuation, nutrient concentrations, chlorophyll) will be provided by the Danish, Swedish and German monitoring programs.

*Work Package 2- Model adaptation and validation (Responsible project partner: NERI).*

The current hydrodynamic model being implemented for the Baltic-North Sea region at NERI in Denmark is COHERENS. COHERENS is a 3-D hydrodynamic model for coastal and shelf seas developed over the period of 1990-1998 by a multinational European group, as part of the MAST projects funded by the European Union. Although the model includes other biological and sediment transport modules, in this project we will only be applying the physical modules for currents, salinity and temperature. At NERI this module is already set up and running for the Baltic Sea study region.

The boundary conditions and atmospheric forcing data for the model are collected and freely available to the project.

The goal of this work package will be to validate the model by comparing the predicted results against the collected data from the monitoring cruises. Once we are satisfied with the models description of the physical water mixing occurring we can proceed with integrating the CDOM optical properties into it (Work Package 3).

*Work Package 3- Integration (Responsible project partner: NERI).*

The final phase of the project will involve the integration of the physical mixing model with our understanding of CDOM properties in these waters. Some initial studies suggest that despite the fact that DOM is a very dynamic component of several biogeochemical cycles, much of its variability in quantity and quality can be explained by conservative mixing (Højerslev et al 1996; Stedmon & Markager 2003; Hansel et al 2004). This is especially true for the months of the year outside of the phytoplankton growth season. During the spring bloom and summer bloom a significant amount of autochthonous CDOM is produced and adds to the background allochthonous signal. Recent work in Polish coastal waters has revealed that these deviations from conservative behavior can easily be modeled (accounted for) by including simple empirically derived models of biological production of CDOM (Kowalczyk et al 2006). A similar approach will be applied in this project. Firstly the properties of the CDOM end members in the mixing zone will be described and placed into the physical mixing model. Model prediction of CDOM distributions and characteristics will then be compared with measured values from WP1 and the degree of conservative mixing assessed. This will allow us to secondly evaluate the scale of impact of the non conservative processes (photochemistry and biological production) and hereafter include them when necessary using a multi-linear regression approach.

## **WORK COMPLETED**

The project officially started in April 2006. A project planning meeting was held at NERI from the 28<sup>th</sup>-30<sup>th</sup> June 2006. Here the projects sampling strategy (cruises) and sampling methods were discussed and agreed upon. The first cruise was 21-27<sup>th</sup> of August 2006 in the Baltic Danish waters (Kattegat, Belt Sea, Sound and Arkona Sea), encompassing around 25 stations and just under 200 samples. Sample measurement of CDOM absorption and fluorescence is completed and the dissolved organic carbon samples are sent to Naval Research Laboratory (Co-PI: C. Osburn) for analysis (DIC/DOC and stable isotopes).

The second cruise is currently underway and will revisit the same stations. The third and final cruise for 2006 is planned for the end of October 2006 and visit the same stations

## **RESULTS**

Due to the early stage of the project there are no results to report of yet (see section above).

## **IMPACT/APPLICATIONS**

The project area is relevant to the three major interest areas of the Ocean, Atmosphere and Space department (Code 32) at ONR: Battlespace Environments, Anti-Submarine Warfare and Mine Warfare.

These three science and technology areas all have a vested interest in underwater optics in the coastal zone. The success of future development and increased application of airborne, satellite and submarine optical sensors in these waters is largely dependent on removing the CDOM signal. Dynamical physical mixing models are already used in a wide range of oceanographic research and monitoring applications, however the use of these for predicting CDOM distributions is not widespread. The proposed biophysical model would generate forecasting and nowcasting data to support the Navy's Littoral Remote Sensing program and FNC Littoral Antisubmarine Warfare as a major improvement in information awareness and characterization of the littoral battlespace, especially in terms of the inherent optical properties (IOPs) of water, or "water clarity." Data and/or forecasts of IOPs, for example, are useful to mission planners needing to predict diver visibility undersea in addition to the efficacy of laser- and camera-based detection systems under variable conditions in the littoral zone.

In the larger scientific community this concept addresses a recent NSF RFP on water cycle science (<http://www.nsf.gov/pubs/2004/nsf04577/nsf04577.htm>), which states an interest in projects addressing "mass and energy transfer across the interfaces between land-atmosphere, land-ocean and ocean-atmosphere."

Finally this project will provide scientists with an improved understanding of CDOMs influence on the underwater light climate in these waters. Current ecological models do not take into account CDOMs effect on light attenuation and hence are not able to reproduce the correct photic depth, leading to elevated areal primary productivity estimates. With increased knowledge of the variability of CDOM and the integration of empirical models derived from this project a better estimation of the photic zone can be made in the models.

## **RELATED PROJECTS**

There is a high degree of synergy between this project and another project held by C. Stedmon funded by the Danish Technical Science Research Council. The project is focused on improving fluorescence characterization methods for CDOM and providing increased insight on the correlations between its chemical and optical properties. Project started in 2005 and ends in 2007, with a budget of 1.4 million DKK (approx. US\$230,000).

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